

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>5</sup> :  C08L 71/12		A1	(11) International Publication Number: WO 91/05016 (43) International Publication Date: 18 April 1991 (18.04.91)
(21) International Application Number: PCT/JP90/00548 (22) International Filing Date: 26 April 1990 (26.04.90)  (30) Priority data: 1/260072 6 October 1989 (06.10.89) JP 1/294953 15 November 1989 (15.11.89) JP  (71) Applicant (for all designated States except US): ASAHI KASEI KOGYO KABUSHIKI KAISHA [JP/JP]; 2-6, Doji-mahama 1-chome, Kita-ku, Osaka-shi, Osaka 530 (JP).  (72) Inventors; and (75) Inventors/Applicants (for US only): AKIYAMA, Yoshikuni [JP/JP]; 1005-1, Higashitomi, Kurashiki-shi, Okayama-ken 710 (JP). MIZUSHIRO, Ken [JP/JP]; 1-6-39, Koremasa, Fuchu-shi, Tokyo 183 (JP).			(74) Common Representative: ASAHI KASEI KOGYO KABUSHIKI KAISHA, Patent Department, Asahi Kasei Kogyo Kabushiki Kaisha, 1-2, Yuraku-cho 1-chome, Chiyoda-ku, Tokyo 100 (JP).  (81) Designated States: CA, DE*, GB, NL, US.  Published With international search report.

(54) Title: A SHAPED RESIN ARTICLE

(57) Abstract

Disclosed is a shaped resin article comprising (1) a continuous phase of a polyphenylene ether and (2) a dispersed phase dispersed in the continuous phase (1). The dispersed phase comprises (a) a particulate dispersed polyolefin phase which is comprised of a polyolefin and has a minor diameter of not greater than 0.5  $\mu\text{m}$ , the outer surface of the dispersed polyolefin phase (a) having, cohered thereto, particles of at least one copolymer selected from the group consisting of a copolymer of a vinyl aromatic compound and a conjugated diene compound and a hydrogenation product thereof, and (b) a particulate dispersed copolymer phase having a minor diameter of not greater than 0.3  $\mu\text{m}$ , which is comprised of at least one copolymer selected from the above-mentioned group and is dispersed in the continuous phase (1) and not cohered to the dispersed polyolefin phase (a). The shaped resin article has not only remarkably improved weld-line toughness and delamination resistance but also excellent resistance to heat, impact and chemicals.



# DESIGNATIONS OF "DE"

Until further notice, any designation of "DE" in any international application whose international filing date is prior to October 3, 1990, shall have effect in the territory of the Federal Republic of Germany with the exception of the territory of the former German Democratic Republic.

## FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MC	Monaco
AU	Australia	FI	Finland	MG	Madagascar
BB	Barbados	FR	France	ML	Mali
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Fasso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GR	Greece	NL	Netherlands
BJ	Benin	HU	Hungary	NO	Norway
BR	Brazil	IT	Italy	PL	Poland
CA	Canada	JP	Japan	RO	Romania
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	LJ	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
DE	Germany	LU	Luxembourg	TD	Chad
DK	Denmark			TC	Togo
				US	United States of America

## DESCRIPTION

## A Shaped Resin Article

## Technical Field

The present invention relates to a shaped resin  
5 article. More particularly, the present invention is  
concerned with a shaped resin article comprising a  
continuous phase of a polyphenylene ether and a dis-  
persed phase dispersed in the continuous phase and  
comprising a particulate dispersed polyolefin phase,  
10 the outer surface thereof having particles of at least  
one specific copolymer cohered thereto, and a particu-  
late dispersed copolymer phase.

The shaped resin article of the present invention  
has excellent weld-line toughness and excellent resist-  
15 ance to delamination, heat, impact and chemicals.  
Accordingly, the shaped resin article of the present  
invention can advantageously be utilized for various  
electrical and electronic components, automobile parts  
and other engineering materials.

## 20 Background Art

Polyphenylene ethers have excellent transparency,  
mechanical and electrical properties, heat resistance  
and dimensional stability as well as advantageously low  
moisture absorption. However, polyphenylene ethers  
25 have poor moldability and poor impact strength.

To obviate the drawbacks of poor moldability and poor impact strength, it has been attempted to blend a polyphenylene ether with a polystyrene or a high impact polystyrene. Compositions comprising a polyphenylene ether and a polystyrene or a high impact polystyrene are now widely used to manufacture electrical and electronic components, housings for business machines, automobile parts, precision components and other engineering materials. With respect to such classical polyphenylene ether resin compositions comprising a polyphenylene ether and a high impact polystyrene, reference is made to, for example, U.S. Patent No. 3,383,435. Such polyphenylene ether resin compositions exhibit improved impact strength. However, they have poor chemical resistance.

Proposals for improving both of impact strength and chemical resistance, especially solvent resistance, by blending a polyphenylene ether with a polyolefin have been made, for which reference is made to, for example, U.S. Patent No. 3,361,851 and Japanese Examined Patent Application Publication Specification No. 42-7069/1967. Compositions comprising a polyphenylene ether and a polyolefin suffer from severe delamination so that the actual application of the compositions is extremely limited.

In the art, other various proposals have also been made. U.S. Patent No. 3,994,856 discloses a composition obtained by blending a polyphenylene ether or a combination of a polyphenylene ether and a polystyrene resin with a hydrogenated block copolymer, which composition is described as exhibiting improved impact resistance and solvent resistance. Further, U.S. Patent No. 4,145,377 discloses a composition comprising a polyphenylene ether or a combination of a polyphenylene ether resin and a polystyrene resin, a preliminary blend of a polyolefin and a hydrogenated block copolymer in weight proportions of 20-80 : 80-20, and a hydrogenated block copolymer, which composition is described as exhibiting improved impact resistance and solvent resistance. Still further, U.S. Patents Nos. 4,166,055; 4,239,573 and 4,242,263, disclose compositions obtained by blending a polyphenylene ether with a block copolymer or with a combination of a hydrogenated block copolymer and a polyolefin, which compositions are described as having improved impact resistance. Still further, U.S. Patent No. 4,383,082, European Patent Publication No. 115,712 and Dutch Patent No. 7,410,861 disclose compositions obtained by blending a polyphenylene ether with a polyolefin and a hydrogenated block copolymer, which compositions are described as having improved impact

resistance. Still further, U.S. Patent No. 4,863,997 and Japanese Patent Application Laid-Open Specifications Nos. 63-113058/1988; 63-225642/1988; 64-98647/1989; 64-204939/1989 and 64-221444/1989 disclose compositions obtained by adding a specific hydrogenated block copolymer to a blend comprising a polyolefin resin and a polyphenylene ether resin, which compositions are described as having improved chemical resistance and moldability. Still further, Japanese Patent Application Laid-Open Specification Nos. 63-218748/1988; 63-245453/1988 and 64-40556/1989 disclose compositions obtained by melt kneading a precompound comprising a specific block copolymer and a polyolefin with a polyphenylene ether, which compositions are described as having improved chemical resistance and moldability. The above-mentioned various polyphenylene ether resin compositions exhibit improved solvent resistance and impact resistance as compared to the conventional polyphenylene ether resin composition comprising a polyphenylene ether and polystyrene or a high impact polystyrene. However, they have inherent problems which limit their applications. In particular, conventional compositions comprising at least 50 % by weight of a polyphenylene ether and up to 20 % by weight of a polyolefin result in a shaped article which

exhibits severe delamination and poor weld-line toughness. Such compositions cannot cope with an increasing demand for higher quality in the art with respect to engineering plastics.

5 Disclosure of The Invention

The present inventors have made extensive and intensive studies with respect to shaped resin articles comprising a polyphenylene ether, a polyolefin and a compatibility agent. As a result, it has been found that a shaped resin article having not only remarkably improved weld-line toughness and delamination resistance but also excellent resistance to heat, impact and chemicals under the application of stress can be obtained by attaining specific morphology of dispersion with respect to the polyolefin and the compatibility agent. Based on this unexpected finding, the present invention has been completed.

It is, therefore, an object of the present invention to provide a shaped resin article comprising a polyphenylene ether, a polyolefin and a compatibility agent, which is free from the drawbacks of the prior art and has not only remarkably improved weld-line toughness and delamination resistance but also excellent resistance to heat, impact and chemicals.

25 The foregoing and other objects, features and

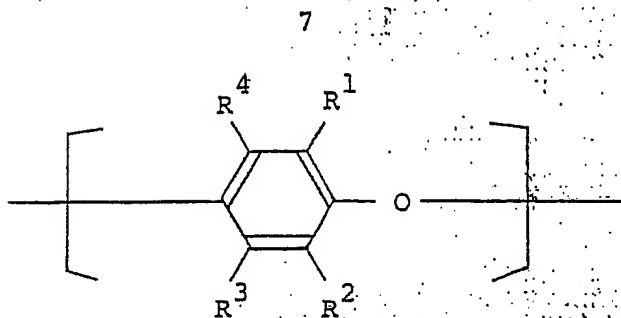


advantages of the present invention will be apparent from the following detailed description and appended claims.

According to the present invention, there is  
5 provided a shaped resin article comprising (1) a continuous phase of a polyphenylene ether and (2) a dispersed phase dispersed in the continuous phase (1). The dispersed phase comprises ( $\alpha$ ) a particulate dispersed polyolefin phase which is comprised of a polyolefin and has a minor diameter of not greater than  
10 0.5  $\mu\text{m}$ , the outer surface of the dispersed polyolefin phase ( $\alpha$ ) having, cohered thereto, particles of at least one copolymer selected from the group consisting of a copolymer of a vinyl aromatic compound and a  
15 conjugated diene compound and a hydrogenation product thereof, and ( $\beta$ ) a particulate dispersed copolymer phase having a minor diameter of not greater than 0.3  $\mu\text{m}$ , which is comprised of at least one copolymer selected from the above-mentioned group and is dis-  
20 persed in the continuous phase (1) and not cohered to the dispersed polyolefin phase ( $\alpha$ ).

The polyphenylene ether (hereinafter frequently referred to simply as "PPE") used for forming the continuous phase in the present invention is a homopolymer or a copolymer having recurring units of the  
25

formula:



wherein each of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  independently represents a hydrogen atom, a halogen atom, a phenyl group, or a group selected from the group consisting of a primary lower alkyl group having from 1 to 7 carbon atoms, a secondary lower alkyl group having from 1 to 7 carbon atoms, a haloalkyl group having from 1 to 7 carbon atoms, an amino alkyl group having from 1 to 7 carbon atoms, a hydrocarbyloxy group having from 1 to 7 carbon atoms and a halohydrocarbyloxy group having from 1 to 7 carbon atoms and having at least two carbon atoms between the halogen atom and the oxygen atom.

The reduced viscosity, as measured at 30 °C with respect to a chloroform solution having a concentration of 0.5 g/dl, of the PPE used in the present invention is generally in the range of from 0.15 to 0.70, preferably from 0.20 to 0.60. Representative examples of the above-mentioned PPE's include poly(2,6-dimethyl-1,4-phenylene ether), poly(2-methyl-6-ethyl-1,4-phenylene ether), poly(2,6-diphenyl-1,4-phenylene ether),

poly(2-methyl-6-phenyl-1,4-phenylene ether), poly(2,6-dichloro-1,4-phenylene ether), a polyphenylene ether copolymer, such as a copolymer of 2,6-dimethyl phenol and another phenol, such as 2,3,6-trimethyl phenol or 2-methyl-6-butyl phenol, and the like. Of these, poly(2,6-dimethyl-1,4-phenylene ether) and a copolymer of 2,6-dimethyl phenol and 2,3,6-trimethyl phenol are preferred, and poly(2,6-dimethyl-1,4-phenylene ether) is most preferred.

The PPE's used in the present invention can readily be produced by conventional methods. For example, a PPE which is produced by the oxidative polymerization of, for example, 2,6-xilenol, in the presence of a catalyst comprised of a complex of a cuprous salt and an amine according to the method of Hay as disclosed in U.S. Patent No. 3,306,874 can advantageously be used in the present invention. Also, the PPE's used in the present invention can readily be produced by the methods as disclosed in U.S. Patent Nos. 3,306,875; 3,257,357 and 3,257,358, Japanese Examined Patent Application Publication Specification No. 52-17880/1977, Japanese Patent Application Laid-Open Specifications Nos. 50-51197/1975 and 63-152628/1988.

In addition to the above-mentioned PPE's, the PPE used in the present invention can be a conventional.

modified PPE which is obtained by reacting a PPE with an  $\alpha$ ,  $\beta$ -unsaturated carboxylic acid or a derivative thereof in the presence or absence of a radical generator at a temperature of 80° to 350 °C in a molten state, a solution state or a slurry state. In this conventional modified PPE, 0.01 to 10 % by weight of an  $\alpha$ ,  $\beta$ -unsaturated carboxylic acid or derivative thereof is bonded to PPE chains by a grafting or addition reaction. Further, the PPE used in the present invention can be a mixture of a PPE selected from the various known PPE's mentioned hereinbefore and the above-mentioned conventional modified PPE in arbitrary proportions.

Also, in the present invention, use can be made of a phosphorous compound-treated PPE as obtained by adding 0.2 to 5 parts by weight of 9, 10-dihydroxy-9-oxa-10-phosphaphenanthrene to 100 parts by weight of a PPE and subjecting the resultant mixture to melt-kneading. The phosphorus compound-treated PPE has an excellent color tone.

The polyolefin forming the particulate dispersed polyolefin phase ( $\alpha$ ) in the shaped resin article of the present invention is a polyolefin which is generally used as a conventional molding material and has a weight average molecular weight of not smaller than

30,000, as measured according to the customary gel permeation chromatography method. Representative examples of polyolefins include a high density polyethylene; an extremely high molecular weight high density polyethylene; a low density polyethylene; a linear low density polyethylene; an extremely low density polyethylene (having a density of less than 0.90); an isotactic polypropylene; poly(4-methyl-1-pentene); polybutene-1; and a copolymer of at least two different compounds selected from the group consisting of  $\alpha$ -olefins (such as ethylene and propylene), ethylenically or acetylenically unsaturated carboxylic acids and derivatives thereof, such as a copolymer of ethylene and butene-1, a copolymer of ethylene and (meth)acrylic acid, a copolymer of ethylene and (meth)acrylic ester, a block or random copolymer of propylene and ethylene, a copolymer of propylene and 1-hexene and a copolymer of propylene and 4-methyl-1-pentene. These polyolefins can be used independently or in combination. Of these polyolefins, polyethylene is preferred. Of polyethylenes, a low density polyethylene, especially a linear low density polyethylene, and a high density polyethylene are more advantageously used.

The copolymer (hereinafter frequently referred to as "compatibility agent") to be cohered to the outer

surface of the particulate dispersed polyolefin phase  
( $\alpha$ ), and to be used for forming the particulate dis-  
persed copolymer phase ( $\beta$ ) in the shaped resin article  
of the present invention, includes a copolymer obtained  
5 by copolymerizing a vinyl aromatic compound with a  
conjugated diene compound, a hydrogenation product of  
the copolymer and a mixture of these. In the hydroge-  
nation product, at least 50 %, preferably at least  
80 %, of the olefinic double bonds attributed to the  
10 copolymerized conjugated diene compound are hydrogenat-  
ed.

The compatibility agent may be a random copolymer,  
a block copolymer, a graft copolymer and a combination  
thereof each having a number average molecular weight  
of not smaller than 50,000, as measured according to  
15 the customary gel permeation chromatography method. Of  
these, such a block copolymer is preferred.

Representative examples of vinyl aromatic com-  
pounds for use in the preparation of the compatibility  
agent include at least one compound selected from the  
20 group consisting of styrene,  $\alpha$ -methylstyrene, vinyltol-  
uene, p-tert-butylstyrene, diphenylethylene and the  
like. Of these, styrene is preferred.

On the other hand, representative examples of  
25 conjugated diene compounds for use in the preparation of

the compatibility agent include at least one compound selected from the group consisting of butadiene, isoprene, 1,3-pentadiene, 2,3-dimethyl-1,3-butadiene and the like. Of these, butadiene, isoprene and a combination thereof are preferred.

The method of preparing the compatibility agent is not critical. For example, a copolymer of styrene and butadiene or a hydrogenation product thereof can readily be produced by the anionic polymerization methods as described in British Patent No. 1,130,770 and U.S. Patent Nos. 3,281,383 and 3,639,517 or as described in British Patent No. 1,020,720 and U.S. Patent Nos. 3,333,024 and 4,501,857.

Of these compatibility agents, a block copolymer of a vinyl aromatic compound and a conjugated diene compound or a hydrogenation product thereof having a Young's modulus of 1,500 kg/cm<sup>2</sup> or more, is especially preferred.

As the compatibility agent, for example, Tufprene<sup>®</sup>, Solprene<sup>®</sup>, Tufdene<sup>®</sup>, Asaprene<sup>®</sup> and Tuftec<sup>®</sup>, which are manufactured and sold by Asahi Chemical Industry Co., Ltd., Japan, are preferably used.

The shaped resin article of the present invention has a specific morphology of dispersion. That is, as

described hereinbefore, in the present invention, the shaped resin article comprises (1) a continuous phase of a polyphenylene ether and (2) a dispersed phase dispersed in the continuous phase (1). The dispersed phase (2) comprises ( $\alpha$ ) a particulate dispersed polyolefin phase which is comprised of a polyolefin and has a minor diameter of not greater than 0.5  $\mu\text{m}$ , the outer surface of the dispersed polyolefin phase ( $\alpha$ ) having cohered thereto particles of at least one copolymer selected from the group consisting of a copolymer of a vinyl aromatic compound and a conjugated diene compound and a hydrogenation product thereof, and ( $\beta$ ) a particulate dispersed copolymer phase having a minor diameter of not greater than 0.3  $\mu\text{m}$ , which is comprised of at least one copolymer selected from the above-mentioned group and is dispersed in the continuous phase (1) and not cohered to the dispersed polyolefin phase ( $\alpha$ ).

The desired effects of the present invention can be attained by realizing the above-mentioned specific morphology of dispersion.

In the present invention, a polyphenylene ether, a polyolefin and at least one copolymer are present in proportions such that the polyolefin and the copolymer are dispersed in the polyphenylene ether to thereby



form the continuous phase (1) and the dispersed phase (2) dispersed therein. Generally, the shaped resin article of the present invention comprises (A) 50 to 95 % by weight, preferably from 50 to 90 % by weight, of polyphenylene ether, (B) up to 20 % by weight, preferably from 5 to 15 % by weight, of polyolefin, and (C) up to 40 % by weight, preferably from 10 to 35 % by weight, of at least one copolymer selected from the group consisting of a copolymer of a vinyl aromatic compound and a conjugated diene compound and a hydrogenation product thereof, wherein the total amount of components (A), (B) and (C) is 100 % by weight. However, the proportions of the polyphenylene ether, the polyolefin and the copolymer are not limited to the above-mentioned ranges as long as the specific morphology of dispersion as defined herein can be attained.

The shaped resin article of the present invention has remarkably improved weld-line toughness and delamination resistance and also excellent resistance to heat, impact and chemicals.

The minor diameters of the particulate dispersed polyolefin phase ( $\alpha$ ) and the particulate dispersed copolymer phase ( $\beta$ ) affect the weld-line toughness and delamination resistance of the shaped article. When the minor diameter of the dispersed polyolefin phase ( $\alpha$ )

exceeds 0.5  $\mu\text{m}$  or when the minor diameter of the dispersed copolymer phase ( $\beta$ ) exceeds 0.3  $\mu\text{m}$ , marked delamination is likely to occur, and weld-line toughness is likely to be extremely poor. On the other hand, the major diameters of the particulate dispersed polyolefin phase ( $\alpha$ ) and the particulate dispersed copolymer phase ( $\beta$ ) are not critical in the present invention, and can widely vary depending on the pressure applied during molding, presence or absence of a plasticizer, etc.

The dispersion morphology of the polyolefin and compatibility agent forming dispersed phases in the polyphenylene ether can generally be observed easily by an electron photomicrograph (magnification: for example, 40,000-fold) of a cross section of the shaped resin article (see Figs. 1 and 2). With respect to each of the dispersed polyolefin phase ( $\alpha$ ) and the dispersed copolymer phase ( $\beta$ ), generally, the ratio of major diameter to minor diameter is not smaller than 1. When the ratio of major diameter to minor diameter is 1, the dispersed phase exhibits a circular form, and when the ratio of major diameter to minor diameter is more than 1, the dispersed phase exhibits a fibril form, a lamella form or a similar form. When the dispersed phase [meaning each of the particulate dispersed polyolefin phase ( $\alpha$ ) and the particulate dis-

persed copolymer phase ( $\beta$ )] has a circular form, the minor diameter is equal to the major diameter, each of which corresponds to the diameter of a circle. On the other hand, when the dispersed phase has a fibril form, a lamella form or a similar form, the terminology "minor diameter" used herein means the maximum of distances between opposite points on the periphery of the fibril form, lamella form or similar form, wherein the opposite points are positioned on opposite sides of a longitudinal axis of the dispersed phase (which is defined as a central line extending along the length of the dispersed phase) and each set of opposite points is positioned on a line perpendicular to the above-mentioned longitudinal axis. In this connection, it should be noted that the minor diameter of the particular dispersed polyolefin phase ( $\alpha$ ) does not include the copolymer particles cohered thereto. When when the dispersed phase has a lamella form, a fibril form or a similar form, the terminology "major diameter" used herein means the maximum of distances between opposite points on the periphery of the fibril form, lamella form or similar form, wherein the opposite points are positioned on opposite sides of a short axis of the dispersed phase (which is defined as a central line extending in a direction perpendicular to the above-

mentioned longitudinal axis) and each set of opposite points is positioned on a line parallel to the above-mentioned longitudinal axis. The expression "the particulate dispersed polyolefin phase ( $\alpha$ ) has a minor diameter of not greater than 0.5  $\mu\text{m}$ " used herein means that at least 90 % of particles of the particulate dispersed polyolefin phase ( $\alpha$ ) have a minor diameter, as defined above, of not greater than 0.5  $\mu\text{m}$ . Likewise, the expression "the particulate dispersed copolymer phase ( $\beta$ ) has a minor diameter of not greater than 0.3  $\mu\text{m}$ " used herein means that at least 90 % of particles of the particulate dispersed copolymer phase ( $\beta$ ) have a minor diameter, as defined above, of not greater than 0.3  $\mu\text{m}$ .

The condition of coherence of the compatibility agent to the outer surface of the dispersed polyolefin phase ( $\alpha$ ) can also easily be observed on an electron photomicrograph (magnification: for example, 40,000-fold) of a cross section of the shaped resin article.

The terminology "cohered" used herein means a configuration in which a number of particles of the compatibility agent gather around and adhere to the outer surface of the dispersed polyolefin phase in the form of isolated particles or in the form of a layer of particles. In this connection, it is noted that in the

cohered configuration, it is possible that some particles of the compatibility agent penetrate the interior of the dispersed polyolefin phase ( $\alpha$ ). The minor diameter of the cohered particles of the compatibility agent is not critical in the present invention. However, it is preferred that the minor diameter be smaller than that of the dispersed polyolefin particles.

In the present invention, as described above, it is essential to realize the specific morphology of dispersion. To attain the specific morphology of dispersion, it is preferred that the above-mentioned polyphenylene ether, polyolefin and compatibility agent be kneaded using a twin or multi-screw extruder into which a kneading block can be incorporated at any portion of the screws, the extruder having the following characteristics:

(1)  $L/D \geq 1.5$ , preferably  $L/D \geq 5$

wherein L represents the length (mm) of the kneading block, and D represents the maximum outer diameter (mm) of the kneading block, and

(2)  $\pi \cdot D' \cdot N/h \geq 50$

wherein  $\pi$  is 3.14,  $D'$  represents the screw outer diameter (mm) in the metering zone, N represents the screw revolution rate (number of revolutions/second), and h represents the depth (mm) of

the groove in the metering zone.

In effecting the kneading, it is preferred that the polyphenylene ether, the polyolefin and the compatibility agent be supplied to the extruder all at one time to effect melt kneading thereof while maintaining a portion of the barrel of the extruder corresponding to the kneading block at a temperature which is not higher than the glass transition temperature (about 210°C) of the PPE.

From the viewpoint of ease in obtaining a shaped resin article having the desired morphology of dispersion, it is preferred to use as the compatibility agent at least one copolymer selected from the group consisting of a copolymer of a vinyl aromatic compound and a conjugated diene compound and a hydrogenation product thereof each having a Young's modulus of 1,500 Kg/cm<sup>2</sup> or higher.

The shaped resin article of the present invention prepared as described above has not only remarkably improved weld-line toughness and delamination resistance but also excellent resistance to heat, impact and chemicals.

In addition to the above-mentioned essential components, the shaped resin article of the present invention may optionally contain other resins such as

polystyrene resins (e.g., polystyrene and high impact polystyrene) and additives such as antioxidants, weathering resistance improvers, nucleating agents for the polyolefin forming the dispersed polyolefin phase ( $\alpha$ ),  
5 lubricants, organic or inorganic fillers and reinforcing materials (e.g., glass fiber, carbon fiber, whisker, mica, talc, calcium carbonate, potassium titanate and wollastonite), fire retardants, plasticizers (e.g., phosphorus compounds such as triphenylphosphate),  
10 colorants, antistatic agents and mold release agents, as long as the characteristic features of the shaped resin article of the present invention are not adversely affected.

The molding method for producing the shaped resin  
15 article of the present invention is not limited as long as in the final shaped resin article the polyolefin and the compatibility agent dispersed in the continuous phase of the polyphenylene ether exhibit the above-mentioned specific dispersion morphology. The shaped  
20 resin article of the present invention may be a pellet. Further, the shaped resin article of the present invention may be a compression-molded article, an injection-molded article, an extrusion-molded article, a blow-molded article or an inflation-molded article, which  
25 article is suitably shaped for an ultimate use.

ASTM Type I dumbbell specimen (thickness: 1/8 inch) for tensile test having a weld-line in the middle portion thereof.

Example 1

5           70 parts by weight of a PPE having a reduced viscosity of 0.56, 10 parts by weight of a low density polyethylene having a density of 0.918 g/cm<sup>3</sup> (Suntec<sup>®</sup> LD-M1804 manufactured and sold by Asahi Chemical Industry Co., Ltd., Japan), 10 parts by weight of a  
10           styrene-butadiene copolymer (Asaflex<sup>®</sup> 810 manufactured and sold by Asahi Chemical Industry Co., Ltd., Japan and having a Young's modulus of 4,600 Kg/cm<sup>2</sup>), 10 parts by weight of a styrene-butadiene copolymer (Solprene<sup>®</sup> T406 manufactured and sold by Japan Elastomer Co.,  
15           Ltd., Japan and having a Young's modulus of 2,100 kg/cm<sup>2</sup>), 1.5 parts by weight of 9,10-dihydro-9-oxa-10-phosphaphenanthrene and 7 parts by weight of triphenylphosphate were blended by a Henschel mixer. The resultant blend was subjected to melt kneading by a same  
20           direction-revolving twin-screw extruder (model PCM-30 manufactured and sold by Ikegai Tekko Co., Ltd., Japan) under conditions such that the kneading block portions of the screws were maintained at 190 °C and the other portions were maintained at 270 °C and that the L/D  
25           ratio, as defined hereinbefore, of each of the kneading



injection molded according to the method as described above, and sliced to obtain a section, which was dyed with osmic acid ( $\text{OsO}_4$ ). The section was photographed by means of a transmission electron microscope to closely examine the dispersion morphology of the test piece (see Fig. 1). As a result, it was found that the test piece had a dispersion morphology such that in the continuous phase of the PPE, low density polyethylene particles having a minor diameter of not greater than 0.5  $\mu\text{m}$  and styrene-butadiene copolymer particles having a minor diameter of not greater than 0.1  $\mu\text{m}$  were dispersed, and that styrene-butadiene copolymer particles were cohered to the outer surface of the dispersed low density polyethylene particles.

#### Comparative Example 1

Melt kneading and injection molding were conducted in substantially the same manner as in Example 1 except that a reverse direction-revolving twin screw extruder (manufactured and sold by Nakatani Kikai K.K., Japan; diameter: 30 mm) was employed, and that the L/D ratio, as defined hereinbefore, of the kneading block was 0 (a kneading block cannot be assembled into the screws of the extruder), the value of  $\pi \cdot D' \cdot N/h$ , as defined hereinbefore, was 36.2 and the extruder was set at 240° to 270 °C, thereby obtaining test pieces for tensile

testing. When the test pieces were subjected to a tensile testing in the same manner as in Example 1, delamination was markedly observed on the surface portion of the cross-section of the test pieces.

5       The weld-line toughness of a test piece having a weld-line was found to be 64 %.

Further, a test piece for tensile testing was injection molded according to the method as described above, and subjected to an examination of the dispersion morphology of the components in the same manner as  
10       in Example 1. As a result, it was found that the test piece had a dispersion morphology such that in the continuous phase of the PPE, low density polyethylene particles having a minor diameter of 0.4 to 1.7  $\mu\text{m}$   
15       (with most of the particles having a minor diameter exceeding 0.5  $\mu\text{m}$ ) and styrene-butadiene copolymer particles having a minor diameter of 0.5 to 1.8  $\mu\text{m}$   
(with most of the particles having a minor diameter exceeding 0.3  $\mu\text{m}$ ) were dispersed, part of the sty-  
20       rene-butadiene copolymer particles being cohered to the outer surface of the low density polyethylene particles.

Examples 2 and 3 and Comparative Examples 2 and 3

76 Parts by weight of a PPE having a reduced  
25       viscosity of 0.49, 8 parts by weight of a high density

polyethylene having a density of  $0.969 \text{ g/cm}^3$  (Suntec<sup>®</sup> HD-J240 manufactured and sold by Asahi Chemical Industry Co., Ltd., Japan), 8 parts by weight of a hydrogenation product of a styrene-butadiene block copolymer (hydrogenation ratio of the polybutadiene segment: 99.9 %; Young's modulus:  $3,200 \text{ kg/cm}^2$ ) and 8 parts by weight of a hydrogenation product of a styrene-butadiene block copolymer (hydrogenation ratio of polybutadiene segments: 99.9 %; Young's modulus:  $5,300 \text{ kg/cm}^2$ ) were blended by a Henschel mixer. The resultant blend was subjected to melt kneading by a same direction-revolving twin-screw extruder (model PCM-30 manufactured and sold by Ikegai Tekko Co., Ltd., Japan) under conditions such that the kneading block portions of the screws were maintained at  $200^\circ\text{C}$  and the other portions were maintained at  $270^\circ\text{C}$ , thereby obtaining strands. In Example 2, the L/D ratio, as defined hereinbefore, was 4.1 and the  $\pi \cdot D' \cdot N/h$  value, as defined hereinbefore, was 94.2. In Example 3, the L/D ratio was 14, and the  $\pi \cdot D' \cdot N/h$  value was 62.9. In Comparative Example 2, the L/D ratio was 2.0, and the  $\pi \cdot D' \cdot N/h$  value was 37.7. In Comparative Example 3, the L/D ratio was 0, and the  $\pi \cdot D' \cdot N/h$  value was 62.9.

The obtained strands were pelletized. The resultant pellets were subjected to injection molding by

means of a screw in-line type injection molding machine having a cylinder temperature of 280° to 300 °C at a mold temperature of 80 °C, thereby obtaining test pieces for tensile testing. Using the test pieces, a tensile testing was conducted in accordance with ASTM D-638 in the same manner as in Example 1. When the cross-section of each of the test pieces obtained in Examples 2 and 3 was examined, no delamination was observed. However, with respect to the test pieces obtained in Comparative Examples 2 and 3, delamination was markedly observed on the cross-section of the test pieces although the test pieces had the same composition as those of Examples 2 and 3.

Further, when the pieces having a weld-line were subjected to a tensile testing, it was found that the test pieces of Examples 2 and 3 had weld-line toughness values of 91 % and 84 %, respectively, and that the test pieces of Comparative Examples 2 and 3 had weld-line toughness values of 71 % and 63 %, respectively.

Further, test pieces for tensile testing were injection molded according to the method as described above and sliced to obtain sections which were dyed with ruthenic acid ( $\text{RuO}_4$ ). The sections were photographed by means of a transmission electron microscope, to closely examine the dispersion morphology of the

test pieces. As a result, it was found that in the test pieces of Examples 2 and 3, high density polyethylene particles having a minor diameter of not greater than 0.5  $\mu\text{m}$  were dispersed in the PPE, whereas in the test piece of Comparative Example 2, high density polyethylene particles having a minor diameter of 0.5  $\mu\text{m}$  to 1.0  $\mu\text{m}$  (with most of the particles having a minor diameter exceeding 0.5  $\mu\text{m}$ ) were dispersed in the PPE and in the test piece of Comparative Example 3, high density polyethylene particles having a minor diameter of 0.5  $\mu\text{m}$  to 2.3  $\mu\text{m}$  (with most of the particles having a minor diameter exceeding 0.5  $\mu\text{m}$ ) were dispersed in the PPE. With respect to each of Examples 2 and 3 and Comparative Examples 2 and 3, particles of the hydrogenation product of a styrene-butadiene block copolymer used as the compatibility agent cohered to the outer surface of the high density polyethylene particles. In Examples 2 and 3, the dispersed particles of the hydrogenated styrene butadiene block copolymer used as the compatibility agent which were not cohered to the dispersed particulate polyethylene phase, had a minor diameter of not greater than 0.1  $\mu\text{m}$ , whereas in Comparative Examples 2 and 3, the dispersed particles of the compatibility agent which were not cohered to the dispersed particulate polyethylene, had

a minor diameter of 0.1 to 0.9  $\mu\text{m}$  (with most of the particles having a diameter exceeding 0.3  $\mu\text{m}$ ).

#### Comparative Example 4

Composition according to U.S. Patent No. 4,145,377

5           A low density polyethylene referred to as component (c1) and a hydrogenated styrene-butadiene-styrene block copolymer referred to as component (c2), as defined in the footnote of Table 1, were melt kneaded in weight proportions indicated in Table 1 at a temperature of from 200° to 240 °C by means of a same direction-revolving twin-screw extruder (model PCM-30 manufactured and sold by Ikegai Tekko Kabushiki Kaisha, Japan), thereby obtaining precompound (P). Then, a polyphenylene ether referred to as component (a), a polystyrene referred to as component (b) and a hydrogenated styrene-butadiene-styrene block copolymer referred to as component (d), as defined in the footnote of Table 1, were melt kneaded in weight proportions indicated in Table 1 with the above-obtained precompound (P) by means of the above-mentioned twin-screw extruder at a temperature of from 230° to 280 °C and at a screw speed of 200 rpm, and extruded, thereby obtaining strands. The thus obtained strands were pelletized, thereby obtaining pellets.

10

15

20

Table 1

Component	Formulation (parts by weight)	
(a)	PPE <sup>a)</sup>	74
(b)	Polystyrene <sup>b)</sup>	8
(c1)	LDPE <sup>c1)</sup>	6
(c2)	HTR <sup>c2)</sup>	6
(d)	HTR <sup>d)</sup>	6

Note: a) polyphenylene ether having a reduced viscosity of 0.57

b) polystyrene, Styron<sup>®</sup> 685 (a product of Asahi Chemical Ind. Co., Ltd., Japan)

c1) low density polyethylene (density: 0.918 g/cm<sup>3</sup>), Suntec<sup>®</sup> LD-M1804

(a product of Asahi Chemical Ind. Co., Ltd., Japan)

c2) hydrogenated styrene-butadiene-styrene block copolymer, Shell Kraton<sup>®</sup> G-1650 (a product of Shell Chemical Co., U.S.A.)

d) same as component (c2)

The thus obtained pellets were charged into a screw in-line type injection molding machine having a cylinder temperature of from 280° to 300 °C, and injection molded at a mold temperature of 80 °C to obtain a test piece for use in tensile testing. A tensile test-

ing was conducted using a test piece in accordance with ASTM D-638. The broken section of the test piece was observed. As a result, a marked delamination was found at the surfaces of the broken sections of the test piece.

5 Further, using a metal mold designed to form a weld-line, a test piece for use in tensile testing was injection molded. A tensile testing of the test piece was conducted in the same manner (ASTM D-638) as mentioned above, and the weld-line toughness as defined  
10 below was determined.

$$\text{Weld-line toughness (\%)} = \frac{\text{tensile strength of a test piece having a weld-line}}{\text{tensile strength of a test piece having no weld-line}} \times 100$$

The weld-line toughness of the test piece was found to  
15 be 66 %.

Still further, a test piece for tensile testing was injection molded according to the method as described above, and a section of the test piece was dyed with ruthenic acid ( $\text{RuO}_4$ ). The section was photo-  
20 graphed using a transmission electron microscope. The electron photomicrograph showed that the outer surface of the dispersed low density polyethylene particles had the hydrogenated styrene-butadiene-styrene block copolymer cohered thereto, and that however, the low density  
25 polyethylene particles were dispersed in the polyph-



nylene ether in minor diameters ranging from 0.8 to 2.9  $\mu\text{m}$  (greater than 0.5  $\mu\text{m}$  and so outside the scope of the present invention) and the hydrogenated styrene-butadiene-styrene block copolymer particles were dispersed in the polyphenylene ether in minor diameters ranging from 0.9 to 2.1  $\mu\text{m}$  (greater than 0.3  $\mu\text{m}$  and so outside the scope of the present invention).

#### Comparative Example 5

Composition according to U.S. Patent No. 4,166,055

A polyphenylene ether referred to as component (a), a low density polyethylene referred to as component (b1), a hydrogenated styrene-butadiene-styrene block copolymer referred to as component (b2) and a triphenyl phosphate referred to as component (c), as defined in the footnote of Table 2, were melt kneaded in weight proportions indicated in Table 2 by means of a same direction-revolving twin-screw extruder (model PCM-30 manufactured and sold by Ikegai Tekko Kabushiki Kaisha, Japan) at a temperature of from 230° to 280 °C and at a screw speed of 200 rpm, and extruded, thereby obtaining strands. The thus obtained strands were pelletized, thereby obtaining pellets.

The thus obtained pellets were charged into a screw in-line type injection molding machine having a cylinder temperature of from 280° to 300 °C, and injec-

tion molded at a mold temperature of 80 °C to obtain a test piece for use in tensile testing. A tensile testing was conducted using a test piece in accordance with ASTM D-638.

5           The broken sections of the test piece were observed. As a result, a marked delamination was found at the surfaces of the broken sections of the test piece.

10           Further, using a metal mold designed to form a weld-line, a test piece for use in tensile testing was injection molded. A tensile testing of the test piece was conducted in the same manner (ASTM D-638) as mentioned above, and the weld-line toughness as defined below was determined.

15           Weld-line           tensile strength of a test  
          toughness (%) =  $\frac{\text{piece having a weld-line}}{\text{tensile strength of a test piece having no weld-line}} \times 100$

The weld-line toughness of the test piece was found to be 59 %.

20           Still further, a test piece for tensile testing was injection molded according to the method as described above, and a section of the test piece was dyed with ruthenic acid ( $\text{RuO}_4$ ), and the section was photographed using a transmission electron microscope. The electron photomicrograph showed that the outer surface  
25           of the dispersed low density polyethylene particles had

the hydrogenated styrene-butadiene-styrene block copolymer cohered thereto, and that, however, the low density polyethylene particles were dispersed in the polyphenylene ether in minor diameters ranging from 1.1 to 2.2  $\mu\text{m}$  (greater than 0.5  $\mu\text{m}$  and so outside the scope of the present invention) and the hydrogenated styrene-butadiene-styrene block copolymer particles were dispersed in the polyphenylene ether in minor diameters ranging from 0.7 to 2.3  $\mu\text{m}$  (greater than 0.3  $\mu\text{m}$  and so outside the scope of the present invention).

#### Comparative Example 6

Composition according to U.S. Patent No. 4,239,673

Substantially the same procedure as described in Comparative Example 5 was repeated except that 12 parts by weight of a styrene-butadiene-styrene block copolymer referred to as component (b3), as defined in the footnote of Table 2, was used instead of a hydrogenated styrene-butadiene-styrene block copolymer, thereby obtaining a test piece. The properties of the test piece were determined in the same manner as described in Comparative Example 5. As a result, a marked delamination was found at the surfaces of the broken sections of the test piece. Further, the weld-line toughness of the test piece was found to be 68 %. Still further, a test piece for tensile testing was injection molded

according to the method as described above, and a section of the test piece was dyed with osmic acid ( $\text{OsO}_4$ ). The section was photographed using a transmission electron microscope. The electron photomicrograph showed that the outer surface of the dispersed low density polyethylene particles had the styrene-butadiene-styrene block copolymer cohered thereto, and that, however, the low density polyethylene particles were dispersed in the polyphenylene ether in minor diameters ranging from 0.8 to 2.5  $\mu\text{m}$  (greater than 0.5  $\mu\text{m}$  and so outside the scope of the present invention) and the styrene-butadiene-styrene block copolymer particles were dispersed in the polyphenylene ether in minor diameters ranging from 0.5 to 2.4  $\mu\text{m}$  (greater than 0.3  $\mu\text{m}$  and so outside the scope of the present invention).

#### Comparative Example 7

Composition according to U.S. Patent No. 4,242,263

Substantially the same procedure as described in Comparative Example 5 was repeated except that 6 parts by weight of the styrene-butadiene-styrene block copolymer referred to as component (b3) was added and the amount of the hydrogenated styrene-butadiene-styrene block copolymer was changed to 6 parts by weight from 12 parts by weight, thereby obtaining test pieces. The

properties of the test pieces were determined in the same manner as described in Comparative Example 5. As a result, a marked delamination was found at the surfaces of the broken sections of a test piece. Further, the weld-line toughness of a test piece was found to be 51 %. Still further, a section of a test piece for tensile testing was dyed with ruthenic acid ( $\text{RuO}_4$ ), and the section was photographed using a transmission electron microscope. The electron photomicrograph showed that the outer surface of the low density polyethylene had the styrene-butadiene-styrene block copolymer and the hydrogenated styrene-butadiene-styrene block copolymer cohered thereto, and that however, the low density polyethylene was dispersed in the polyphenylene ether in minor diameters ranging from 1.3 to 2.6  $\mu\text{m}$  (greater than 0.5  $\mu\text{m}$  and so outside the scope of the present invention) and the styrene-butadiene-styrene block copolymer and the hydrogenated styrene-butadiene-styrene block copolymer were dispersed in the polyphenylene ether in minor diameters ranging from 1.1 to 2.8  $\mu\text{m}$  (greater than 0.3  $\mu\text{m}$  and so outside the scope of the present invention).

Table 2

Com- ponent	Formulation (parts by weight)			
		Compara- tive Example 5	Compara- tive Example 6	Compara- tive Example 7
(a)	PPE <sup>a)</sup>	82	82	82
(b1)	LDPE <sup>b1)</sup>	6	6	6
(b2)	HTR <sup>b2)</sup>	12	-	6
(b3)	TR <sup>b3)</sup>	-	12	6
(c)	TFP <sup>c)</sup>	15	15	15

Note: a) polyphenylene ether having a reduced viscosity of 0.57

b1) low density polyethylene (density: 0.918 g/cm<sup>3</sup>), Suntac<sup>®</sup> LD-M1804

(a product of Asahi Chemical Ind. Co., Ltd., Japan)

b2) hydrogenated styrene-butadiene-styrene block copolymer, Shell Kraton<sup>®</sup> G-1650 (a product of Shell Chemical Co., U.S.A.)

b3) styrene-butadiene-styrene block copolymer, Shell Kraton<sup>®</sup> D-1011 (a product of Shell Chemical Co., U.S.A.)

c) triphenyl phosphate (plasticizer)

Comparative Example 8

Composition according to Japanese Patent Application

Laid-Open Specification Nos. 63-218748 (1988), 63-245453 (1988) and 64-40556 (1989)

A low density polyethylene referred to as component (c1) and a styrene-butadiene radial teleblock copolymer referred to as component (c2), as defined in the footnote of Table 3, were melt kneaded in weight proportions indicated in Table 3 at a temperature of from 200° to 240 °C by means of a same direction-revolving twin-screw extruder (model PCM-30 manufactured and sold by Ikegai Tekko Kabushiki Kaisha, Japan), thereby obtaining precompound (P). Then, a polyphenylene ether referred to as component (a) and a polystyrene referred to as component (b), as defined in the footnote of Table 3, were melt kneaded in weight proportions indicated in Table 3 with the above-obtained precompound (P) by means of the above-mentioned twin-screw extruder at a temperature of from 230° to 280 °C and at a screw revolving speed of 200 rpm, and extruded, thereby obtaining strands. The thus obtained strands were pelletized, thereby obtaining pellets.

Table 3

Component	Formulation (parts by weight)	
(a)	PPE <sup>a)</sup>	72
(b)	Polystyrene <sup>b)</sup>	16
(c1)	LDPE <sup>c1)</sup>	6
(c2)	TR <sup>c2)</sup>	6
		} premixed

Note: a) polyphenylene ether having a reduced viscosity of 0.57

b) polystyrene, Styron<sup>®</sup> 685 (a product of Asahi Chemical Ind. Co., Ltd., Japan)

c1) low-density polyethylene having a density of 0.918 g/cm<sup>3</sup>, Suntec<sup>®</sup> LD-M1804 (a product of Asahi Chemical Ind. Co., Ltd., Japan)

c2) styrene-butadiene radial teleblock copolymer (Young's modulus: 3,200 Kg/cm<sup>2</sup>)

The thus obtained pellets were charged into a screw in-line type injection molding machine having a cylinder temperature of from 280° to 300 °C, and injection molded at a mold temperature of 80 °C to obtain a test piece for use in tensile testing. A tensile testing was conducted using a test piece in accordance with ASTM D-638. The broken section of the test piece was observed. As a result, no delamination was found at the surfaces of the broken sections of the test



piece.

Further, using a metal mold designed to form a weld-line, a test piece for use in tensile testing was injection molded. A tensile testing of the test piece was conducted in the same manner (ASTM D-638) as mentioned above, and the weld-line toughness as defined below was determined.

$$\text{Weld-line toughness (\%)} = \frac{\text{tensile strength of a test piece having a weld-line}}{\text{tensile strength of a test piece having no weld-line}} \times 100$$

The weld-line toughness of the test piece was found to be 72 %.

Still further, a test piece for tensile testing was injection molded according to the method as described above, and a section of the test piece was dyed with osmic acid ( $\text{OsO}_4$ ). The section was photographed using a transmission electron microscope. The electron photomicrograph showed that the low density polyethylene particles were dispersed in the polyphenylene ether in minor diameters ranging from 0.3 to 1.1  $\mu\text{m}$  (most of the particles having minor diameters of greater than 0.5  $\mu\text{m}$  and so outside the scope of the present invention), and the outer surface of the dispersed low density polyethylene particles had the styrene-butadiene radial teleblock copolymer cohered thereto in the

form of a layer and no styrene-butadiene radial tele-block copolymer having a minor diameter of not greater than 0.3  $\mu\text{m}$  was independently dispersed in the polyphenylene ether.

5 Examples 4 to 6

Each of the compositions indicated in Table 4 was melt kneaded by means of the same direction-revolving twin-screw extruder (model PCM-30 manufactured and sold by Ikegai Tekko Kabushiki Kaisha, Japan) as described in Example 1 under the same conditions as described in Example 1, thereby obtaining strands. The thus obtained strands were pelletized, thereby obtaining pellets.

Table 4

Component	Formulation (parts by weight)			
		Example 4	Example 5	Example 6
(a)	PPE <sup>a)</sup>	66	63	78
(b)	HDPE <sup>b)</sup>	5	10	7
(c)	HTR <sup>c)</sup>	29	27	15
(d)	TPP <sup>d)</sup>	-	-	15

Note: a) polyphenylene ether having a reduced viscosity of 0.54

b) high-density polyethylene (density:

0.918  $\text{g}/\text{cm}^3$ ), Suntec<sup>®</sup> J240 (a

product of Asahi Chemical Ind. Co., Ltd.,  
Japan)

c) hydrogenated styrene-butadiene-styrene block  
copolymer (Young's modulus: 5,100 kg/cm<sup>2</sup>,  
ratio of hydrogenation: 99.9 %)

d) triphenyl phosphate (plasticizer)

The thus obtained pellets were charged into a screw  
in-line type injection molding machine having a cylinder  
temperature of from 280° to 300 °C, and injection  
molded at a mold temperature of 80 °C to obtain test  
pieces for use in tensile testing. A tensile testing  
was conducted using each of the test pieces in accordance  
with ASTM D-638. The broken sections of each of  
the test pieces were observed. As a result, no delamination  
was found at the surfaces of the broken sections  
of each of the test pieces of Examples 4 to 6.

Further, using a metal mold designed to form a  
weld-line, test pieces for use in tensile testing were  
injection molded. A tensile testing of the test pieces  
was conducted in the same manner (ASTM D-638) as mentioned  
above, and the weld-line toughness as defined  
below was determined.

$$\text{Weld-line toughness (\%)} = \frac{\text{tensile strength of a test piece having a weld-line}}{\text{tensile strength of a test piece having no weld-line}} \times 100$$

The weld-line toughness of each of the test pieces of Examples 4 to 6 was found to be 100 %.

Still further, a test piece for tensile testing was injection molded according to the method as described above, and a section of each of the test pieces for tensile testing was dyed with ruthenic acid ( $\text{RuO}_4$ ). The section was photographed using a transmission electron microscope. As a result, it was found that each of the test pieces of Examples 4 to 6 (see Fig. 2 for the dispersion morphology of the cross section of the test piece of Example 5) had a morphology of dispersion such that the high density polyethylene particles were dispersed in a minor diameter of not greater than  $0.5 \mu\text{m}$  and the hydrogenated block copolymer of styrene and butadiene was cohered to the outer surface of the dispersed high density polyethylene phase in the form of a layer of particles. The hydrogenated block copolymer of styrene and butadiene, which was independently dispersed in the polyphenylene ether, had a minor diameter of not greater than  $0.1 \mu\text{m}$ .

#### Examples 7 to 9

Each of the compositions indicated in Table 5 was melt kneaded by means of the same direction-revolving twin-screw extruder (model PCM-30 manufactured and sold by Ikegai Tekko Kabushiki Kaisha, Japan) as described

in Example 1 under the same conditions as described in Example 1, thereby obtaining strands. The thus obtained strands were pelletized, thereby obtaining pellets.

Table 5

Component	Formulation (parts by weight)			
		Example 7	Example 8	Example 9
(a)	PPE <sup>a)</sup>	55	80	86
(b)	PP <sup>b)</sup>	15	5	7
(c1)	HTR <sup>c1)</sup>	30	15	-
(c2)	HTR <sup>c2)</sup>	-	-	7
(d)	TPP <sup>d)</sup>	-	15	15

Note: a) polyphenylene ether having a reduced viscosity of 0.41

b) polypropylene, E-1100 (a product of Asahi Chemical Ind. Co., Ltd., Japan)

c1) hydrogenated styrene-butadiene-styrene block copolymer (Young's modulus: 6,300 kg/cm<sup>2</sup>, ratio of hydrogenation: 99.9 %)

c2) hydrogenated styrene-butadiene-styrene block copolymer (Young's modulus: 4,800 kg/cm<sup>2</sup>, ratio of hydrogenation: 99.9 %)

d) triphenyl phosphate (plasticizer)

The thus obtained pellets were charged into a screw

in-line type injection molding machine having a cylinder temperature of from 280° to 300 °C, and injection molded at a mold temperature of 80 °C to obtain test pieces for use in tensile testing. A tensile testing was conducted using the test pieces in accordance with ASTM D-638. The broken sections of the test pieces were observed. As a result, no delamination was found at the surfaces of the broken sections of each of the test pieces of Examples 7 to 9.

Further, using a metal mold designed to form a weld-line, test pieces for use in tensile testing were injection molded. A tensile testing of the test pieces was conducted in the same manner (ASTM D-638) as mentioned above, and the weld-line toughness as defined below was determined.

$$\text{Weld-line toughness (\%)} = \frac{\text{tensile strength of a test piece having a weld-line}}{\text{tensile strength of a test piece having no weld-line}} \times 100$$

The weld-line toughness of each of the test pieces of Examples 7 to 9 was found to be 100 %.

Still further, test pieces for tensile testing were injection molded according to the method as described above, and sections of the test pieces were dyed with ruthenic acid ( $\text{RuO}_4$ ). The sections were photographed using a transmission electron microscope.

As a result, it was found that each of the test pieces of Examples 7 to 9 had a morphology of dispersion such that the polypropylene particles were dispersed in a minor diameter of not greater than 0.5  $\mu\text{m}$  and the hydrogenated block copolymer of styrene and butadiene was cohered to the outer surface of the dispersed polypropylene phase in the form of a layer of particles. The hydrogenated block copolymer of styrene and butadiene, which was independently dispersed in the polyphenylene ether, had a minor diameter of not greater than 0.1  $\mu\text{m}$ .

#### Examples 10 to 12

Each of the compositions indicated in Table 6 was melt-kneaded by means of the same direction-revolving twin-screw extruder (model PCM-30 manufactured and sold by Ikegai Tekko Kabushiki Kaisha, Japan) as described in Example 1 under the same conditions as described in Example 1, thereby obtaining strands. The thus obtained strands were pelletized, thereby obtaining pellets.

Table 6

Component	Formulation (parts by weight)			
		Example 10	Example 11	Example 12
(a)	PPE <sup>a</sup> )	55	75	84
(b1)	PP <sup>b1</sup> )	7	-	-
(b2)	LDPE <sup>b2</sup> )	8	10	8
(c1)	HTR <sup>c1</sup> )	30	15	-
(c2)	HTR <sup>c2</sup> )	-	-	8
(d)	TPP <sup>d</sup> )	-	15	15

Note: a) polyphenylene ether having a reduced viscosity of 0.41

b1) polypropylene, E-1100 (a product of Asahi Chemical Ind. Co., Ltd., Japan)

b2) low density polyethylene having a density of 0.918 g/cm<sup>3</sup>, Suntec<sup>®</sup> LD-M1804 (a product of Asahi Chemical Ind. Co., Ltd., Japan)

c1) hydrogenated styrene-butadiene-styrene block copolymer (Young's modulus: 5,800 kg/cm<sup>2</sup>, ratio of hydrogenation: 99.9 %)

c2) hydrogenated styrene-butadiene-styrene block copolymer (Young's modulus: 4,800 kg/cm<sup>2</sup>, ratio of hydrogenation: 99.9 %)

d) triphenyl phosphate (plasticizer)

The thus obtained pellets were charged into a screw



in-line type injection molding machine having a cylinder temperature of from 280° to 300 °C, and injection molded at a mold temperature of 80 °C to obtain test pieces for use in tensile testing. A tensile testing was conducted using the test pieces in accordance with ASTM D-638. The broken sections of the test pieces were observed. As a result, no delamination was found at the surfaces of the broken sections of each of the test pieces of Examples 10 to 12.

Further, using a metal mold designed to form a weld-line, test pieces for use in tensile testing were injection molded. A tensile testing of the test pieces was conducted in the same manner (ASTM D-638) as mentioned above, and the weld-line toughness as defined below was determined.

$$\text{Weld-line toughness (\%)} = \frac{\text{tensile strength of a test piece having a weld-line}}{\text{tensile strength of a test piece having no weld-line}} \times 100$$

The weld-line toughness of each of the test pieces of Examples of 10 to 12 was found to be 100 %.

Still further, test pieces for tensile testing were injection molded according to the method as described above, and sections of the test pieces were dyed with ruthenic acid ( $\text{RuO}_4$ ). The sections were photographed using a transmission electron microscope.

As a result, it was found that each of the test pieces of Examples 10 to 12 had a morphology of dispersion such that the polypropylene and low density polyethylene particles were dispersed in a minor diameter of not greater than 0.5  $\mu\text{m}$  and the hydrogenated block copolymer of styrene and butadiene was cohered to the outer surface of the dispersed polypropylene phase in the form of a layer of particles. The hydrogenated block copolymer of styrene and butadiene, which was independently dispersed in the polyphenylene ether, had a minor diameter of not greater than 0.1  $\mu\text{m}$ .

#### Example 13

65 parts by weight of a polyphenylene ether having a reduced viscosity of 0.54, 15 parts by weight of a linear low density polyethylene (Suntec<sup>®</sup> LL-LM7625 having a density of 0.926 g/cm<sup>3</sup> and manufactured and sold by Asahi Chemical Industry Co., Ltd., Japan), 10 parts by weight of a hydrogenated copolymer of styrene and butadiene (Young's modulus: 4,800 kg/cm<sup>2</sup>, ratio of hydrogenation: 99.9 %) and 10 parts by weight of a copolymer of styrene and butadiene (Young's modulus: 2,100 kg/cm<sup>2</sup>, Solprene<sup>®</sup> T406 manufactured and sold by Japan Elastomer Co., Ltd., Japan), were mixed together by means of a Henschel mixer. The obtained mixture was melt kneaded by means of the same extruder as described

in Example 1 under the same conditions as described in Example 1, thereby obtaining strands. The thus obtained strands were pelletized, thereby obtaining pellets. A section of the thus obtained pellets was  
5 dyed with ruthenic acid ( $\text{RuO}_4$ ), and the section was photographed using a transmission electron microscope. As a result, it was found that the pellets had a morphology of dispersion such that the linear low density polyethylene was dispersed in a minor diameter of not  
10 greater than  $0.5\text{ }\mu\text{m}$ , and the block copolymer as a compatibility agent was melted into the dispersed linear low density polyethylene and cohering to the outer surface of the dispersed linear low density polyethylene in the form of a layer of particles. The  
15 block copolymer, which was independently dispersed in the polyphenylene ether, had a minor diameter of not greater than  $0.1\text{ }\mu\text{m}$ .

#### Example 14

The pellets obtained in Example 1 were charged  
20 into a screw in-line type injection molding machine having a cylinder temperature of from  $280^\circ$  to  $300^\circ\text{C}$ , and injection molded at a mold temperature of  $90^\circ\text{C}$  to obtain a test piece for use in the determination of heat deformation temperature. The heat deformation  
25 temperature of the test piece was determined in accord-

ance with ASTM D-648, and was found to be 119 °C.

Further, substantially the same procedure as described above was repeated to obtain a test piece having a thickness of 1/8 inch for use in an Izod impact test. The Izod impact test was conducted at 23 °C using the test piece in accordance with ASTM D-256, and the Izod impact strength was found to be 42 kg·cm/cm.

Still further, in accordance with the Bergen 1/4 ellipse method (see SEP Journal, 667, 1962), a salad oil was applied to the surface of the test piece for use in the Izod test impact test, and then, the strain at the time when crack occurred was determined at 80°C. As a result, the critical strain was found to be 0.5 %.

#### Brief Description of the Drawings

Fig. 1 is an electron photomicrograph showing the morphology of dispersion of the shaped resin article of the present invention as obtained in Example 1; and

Fig. 2 is an electron photomicrograph showing the morphology of dispersion of the shaped resin article of the present invention as obtained in Example 5.

#### Industrial Applicability

The shaped resin article of the present invention has not only remarkably improved weld-line toughness and delamination resistance but also excellent resist-

ance to heat, impact and chemicals. Therefore, the shaped resin article of the present invention is useful as various parts. Representative examples of such parts include automobile parts, e.g., exterior parts such as bumpers, fenders, door panels, various moles, emblems, engine hoods, wheel caps, roofs and spoilers, and interior parts such as instrument panels, console boxes and trims. Further, the shaped resin article of the present invention can also suitably be used as interior and exterior parts of electrical appliances. Representative examples of such exterior and interior parts include cabinets for office automation machines, television sets, video units, TV game sets and various disc players, and parts of refrigerators and the like.

## CLAIMS

1. A shaped resin article comprising:

(1) a continuous phase of a polyphenylene ether  
and (2) a dispersed phase dispersed in said continuous  
phase (1) and comprising :

( $\alpha$ ) a particulate dispersed polyolefin phase which  
is comprised of a polyolefin and has a minor diameter  
of not greater than 0.5  $\mu\text{m}$ , the outer surface of said  
dispersed polyolefin phase ( $\alpha$ ) having, cohered thereto,  
particles of at least one copolymer selected from the  
group consisting of a copolymer of a vinyl aromatic  
compound and a conjugated diene compound and a hydroge-  
nation product thereof, and

( $\beta$ ) a particulate dispersed copolymer phase having  
a minor diameter of not greater than 0.3  $\mu\text{m}$ , which is  
comprised of said at least one copolymer and is dis-  
persed in said continuous phase (1) and not cohered to  
said dispersed polyolefin phase ( $\alpha$ ).

2. The article according to claim 1, wherein said  
particulate dispersed copolymer phase ( $\beta$ ) has a minor  
diameter of not greater than 0.1  $\mu\text{m}$ .

3. The article according to claim 1 or 2, wherein said  
at least one copolymer has a Young's modulus of at

least 1500 Kg/cm<sup>2</sup>.

5           4. The article according to any one of claims 1 to 3,  
          wherein said copolymer of a vinyl aromatic compound and  
          a conjugated diene compound is a copolymer comprising  
          at least one vinyl aromatic compound block and at least  
          one conjugated diene compound block.

10           5. The article according to any one of claims 1 to 3,  
          wherein said hydrogenation product is a hydrogenation  
          product of a copolymer comprising at least one vinyl  
          aromatic compound block and at least one conjugated  
          diene compound block.

15           6. The article according to any one of claims 1 to 5,  
          wherein said polyolefin is a low density polyethylene  
          or a high density polyethylene.

20           7. The article according to claim 6, wherein said  
          polyolefin is a linear low density polyethylene.

25           8. The article according to any one of claims 1 to 7,  
          which is a compression-molded article, an injection-  
          molded article, an extrusion-molded article, a blow-  
          molded article or an inflation-molded article.

9. The article according to any one of claims 1 to 7,  
which is a pellet.

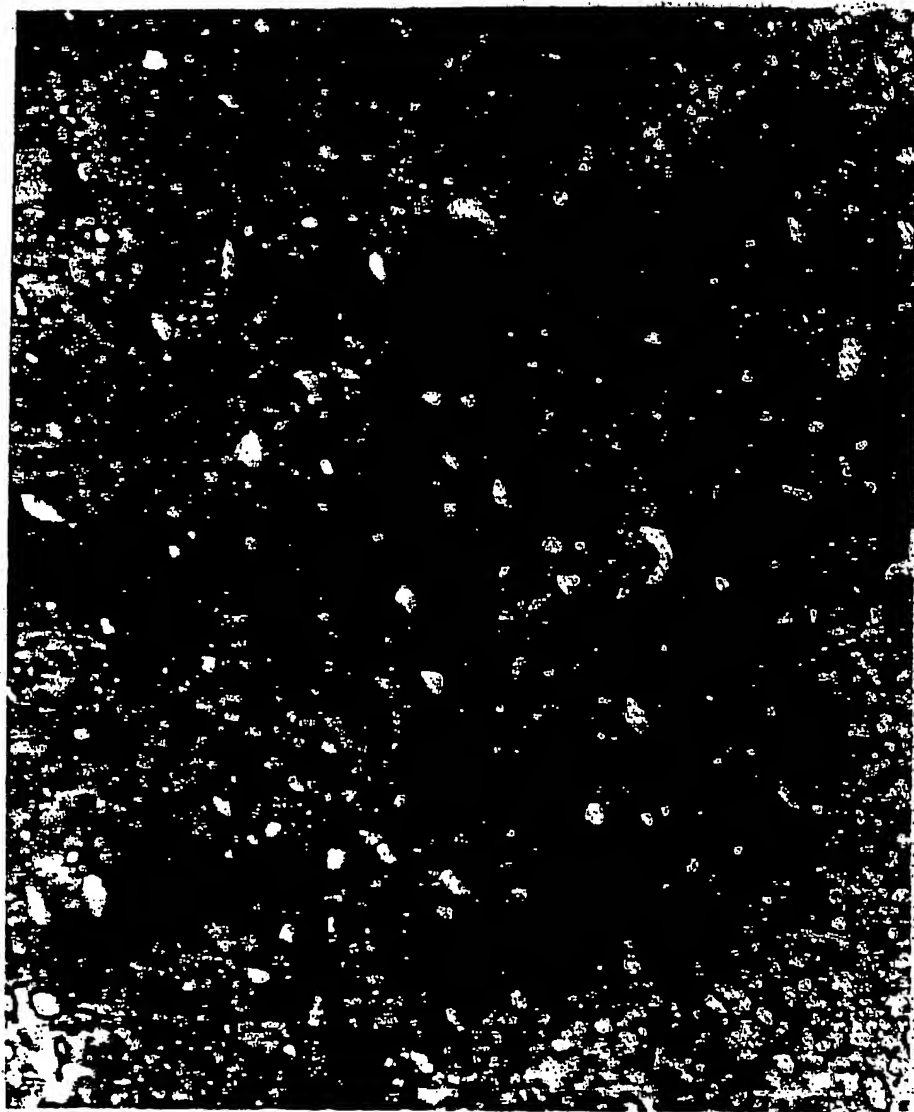


1/2  
FIG.1



0.25  $\mu\text{m}$

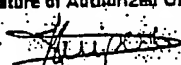
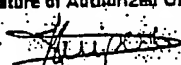
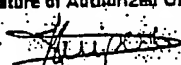
2 / 2  
FIG. 2



0.25  $\mu\text{m}$

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/JP 90/00548

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC <b>IPC5: C 08 L 71/12</b>														
<b>II. FIELDS SEARCHED</b> <div style="text-align: center;">Minimum Documentation Searched<sup>7</sup></div> <table style="width: 100%; border: none;"> <tr> <td style="width: 25%; border: none;">Classification System</td> <td style="border: none;">Classification Symbols</td> </tr> <tr> <td style="border: none; height: 40px; vertical-align: bottom;">IPC5</td> <td style="border: none; vertical-align: bottom;">C 08 L</td> </tr> </table> <div style="text-align: center; font-size: small;">Documentation Searched other than Minimum Documentation to the extent that such Documents are included in Fields Searched<sup>8</sup></div>			Classification System	Classification Symbols	IPC5	C 08 L								
Classification System	Classification Symbols													
IPC5	C 08 L													
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category<sup>10</sup></th> <th style="width: 60%;">Citation of Document,<sup>11</sup> with indication, where appropriate, of the relevant passages<sup>12</sup></th> <th style="width: 30%;">Relevant to Claim No.<sup>13</sup></th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>EP, A2, 0329423 (SUMITOMO CHEMICAL COMPANY, LIMITED) 23 August 1989, see claims 4-10, abstract page 15  --</td> <td style="text-align: center; vertical-align: top;">1-9</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>EP, A2, 0326895 (GENERAL ELECTRIC COMPANY) 9 August 1989, see the abstract, claims 1-9  --</td> <td style="text-align: center; vertical-align: top;">1-9</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>US, A, 4863997 (N. SHIBUYA ET AL.) 5 September 1989, see the abstract, claims 1-14  --</td> <td style="text-align: center; vertical-align: top;">1-9</td> </tr> </tbody> </table>			Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	A	EP, A2, 0329423 (SUMITOMO CHEMICAL COMPANY, LIMITED) 23 August 1989, see claims 4-10, abstract page 15  --	1-9	A	EP, A2, 0326895 (GENERAL ELECTRIC COMPANY) 9 August 1989, see the abstract, claims 1-9  --	1-9	A	US, A, 4863997 (N. SHIBUYA ET AL.) 5 September 1989, see the abstract, claims 1-14  --	1-9
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>												
A	EP, A2, 0329423 (SUMITOMO CHEMICAL COMPANY, LIMITED) 23 August 1989, see claims 4-10, abstract page 15  --	1-9												
A	EP, A2, 0326895 (GENERAL ELECTRIC COMPANY) 9 August 1989, see the abstract, claims 1-9  --	1-9												
A	US, A, 4863997 (N. SHIBUYA ET AL.) 5 September 1989, see the abstract, claims 1-14  --	1-9												
<div style="display: flex; justify-content: space-between; font-size: small;"> <div style="width: 45%;"> <p><b>* Special categories of cited documents:</b><sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 50%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </div> </div>														
<b>IV. CERTIFICATION</b> <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border: none;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="border: none; text-align: center;">18th July 1990</td> <td style="border: none; text-align: center;">27 JUL 1990</td> </tr> <tr> <td style="border: none;">International Searching Authority</td> <td style="border: none;">Signature of Authorized Officer</td> </tr> <tr> <td style="border: none; text-align: center;">EUROPEAN PATENT OFFICE</td> <td style="border: none; text-align: center;">  <b>Mme N. KUIPER</b> </td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	18th July 1990	27 JUL 1990	International Searching Authority	Signature of Authorized Officer	EUROPEAN PATENT OFFICE	 <b>Mme N. KUIPER</b>				
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report													
18th July 1990	27 JUL 1990													
International Searching Authority	Signature of Authorized Officer													
EUROPEAN PATENT OFFICE	 <b>Mme N. KUIPER</b>													

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	US, A, 4617346 (N. SONODA) 14 October 1986, see the abstract, claims 1-9 --	1-9
A	US, A, 4528327 (G.D. COOPER ET AL.) 9 July 1985, see the abstract, claims 1-21 -- -----	1-9

# ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. PCT/JP 90/00548

SA

36313

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 04/07/90. The European Patent office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A2- 0329423	23/08/89	JP-A- 1207349 JP-A- 1234462	21/08/89 19/09/89
EP-A2- 0326895	09/08/89	NONE	
US-A- 4863997	05/09/89	EP-A- 0263678 JP-A- 63225642 JP-A- 63113058	13/04/88 20/09/88 18/05/88
US-A- 4617346	14/10/86	CA-A- 1242041 JP-A- 60155260	13/09/88 15/08/85
US-A- 4528327	09/07/85	AU-D- 8004882 CA-A- 1141064 EP-A- 0054900 WO-A- 82/02208	20/07/82 08/02/83 30/06/82 08/07/82

For more details about this annex: see Official Journal of the European patent Office, No. 12/82